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THE CORROSION OF METALS IN
ORGANIC ACIDS

BY

JOHN BRADSHAW TAYLOR

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED The Corrosion of Metals in Organic Acids.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science.

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J. H. Reedy,
Instructor in Charge

APPROVED:

W. A. Noyes

HEAD OF DEPARTMENT OF


Chemistry

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THE CORROSION OF METALS IN ORGANIC ACIDS.

I

Introduction.

The corrosion of metals in organic acids is of importance in deciding the material most suitable for containers and apparatus for the handling of fruit juices, canned fruits, and milk etc. In an extensive collection of data from many analyses¹ it has been shown that tartaric, malic, succinic, and citric acids are found in fruits to the exclusion of almost all others. The acids investigated in this work are confined to the acids found in fruits. The toxicity of the metal salts and the resistance of the metals to corrosion must be taken into consideration. In general copper is more toxic than tin and tin more toxic than zinc, though the toxicity may change with the particular salt formed.

The amount of corrosion is commonly said to vary or be influenced by several conditions:

1.- The facts of corrosion are often explained by employing the electrolytic potentials of the metals. A more electro negative metal, (using the convention adopted by the American Electrochemical Society) is supposed to corrode more than one that is less electro-negative. Thus the electronegativity or electrolytic solution pressure is a measure of the tendency to form positive ions, leaving the metals negatively charged.

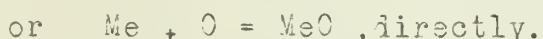
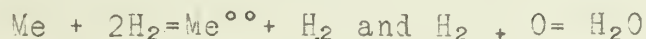
2.- The physical treatment of the metal influences corrosion. Any bending or twisting will usually cause increased corrosion at

the point so strained.

3.- The effect of impurities in metals may increase or decrease the corrosion, depending (as it is usually explained) on whether their effect is to make the metal itself more or less electro-negative.

4.- The effect of corrosion products is recognized to be an important item in corrosion, but the specific cause is rather vague. The setting up of a "galvanic cell" is used by Richardson² in explaining the effect of iron rust in increasing corrosion. Bailey³ in his work with aluminium has noticed the opposite or protective effect of the oxide coating formed.

5.- Dissolved atmospheric oxygen may either attack the metal directly or assist in attack by removal of hydrogen. That is, a metal may corrode in either or both of two ways.



6.- The structure of the acid may also affect the amount of corrosion.

The present work has been carried on in order to find the metal most resistant to corrosion of those tested, and to investigate the possible effects of the amino group and of the number of hydroxyl groups on the amount of corrosion.

II

Historical.

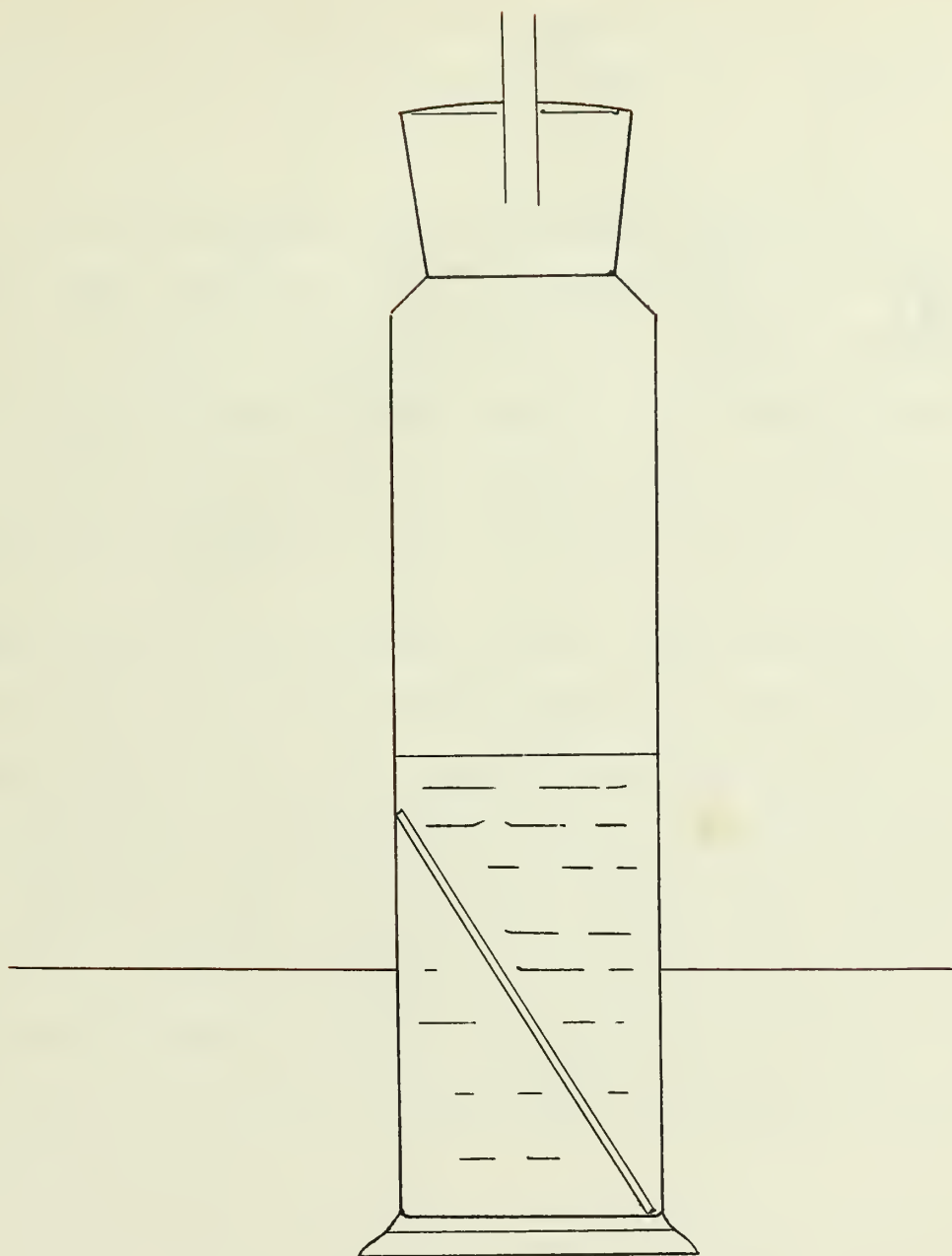
The corrosion of metals in dilute organic acids has been investigated (1921) by Jean C. Shepherd. An attempt to measure the comparative rate of corrosion was made by immersing the metal in the

form of strips in a solution contained in cells with mercury manometer attachments. This afforded a means of detecting any absorption of oxygen or evolution of hydrogen, and thus a measure of the rate of corrosion, by noting the difference in level of the mercury. Readings were made every day for ten days. The atmosphere above the liquid was sparked to determine any hydrogen evolved. In this way it was hoped to ascertain the true amount of oxygen absorbed. Zinc, tin, copper, and aluminium were tested in propionic, tartaric, citric, and in alanine. This method apparently should have been very reliable, but the results obtained, though admitting of some comparisons, were of almost no value. The chief reason for this probably lies in the fact that the sparking of the hydrogen when it is present in very small amounts is uncertain. Further explanation is found in certain conclusions drawn as a result of this work.

III Experimental.

(a) Method-

The method used here consisted in weighing the strip of metal before immersing in the reagent. On removal, after careful cleaning, drying, and reweighing, the loss in weight was a measure of the amount of corrosion. Zinc, tin, copper, and aluminium strips were used all having the same surface area = 18.9 sq. cm. They were all approximately 5.5 cm. long, 1.7 cm. wide, and 0.15 cm. thick. After cutting to this size the strips were polished with fine emery to make the surfaces as uniform as possible. These were immersed in a cell or bottle with 50 c.c. of the acid solution (see fig. 1) and placed on a



Corrosion Bottle — Fig 1.



shaking platform to gently agitate the liquid. At the end of a period of seven days the strips were taken out, dried, and afterwards cleaned with a soft bristle brush to remove any products of corrosion.

A few difficulties were encountered in making the tests. The acids used would form mould on standing for a few days and thymol was successfully used to prevent this. However when copper was tested in tartaric and in malic acids a black tarry deposit was formed on the metal and on the sides of the cell. This gave no test for copper, was soluble in ether or benzene, and was presumably a formation caused from or by the thymol. This was shown to be the case by trying fresh acid without thymol. No tarry deposit was given and the corrosion loss was less. No reason could be found for the formation with copper nor for its absence with the other metals. Formaline (four drops to 500 c.c. sol.) was substituted for thymol and no further trouble was had. Both thymol and formaline were tested for their corrosive effect on the metals by immersing in pure water as well as in pure water plus thymol or formaline. It was found to be nil.

(2) Results-

TARTARIC ACID.

Zinc in tartaric acid formed a white product which adhered to the strips and which was easily brushed off after drying. The amount of corrosion varied with the concentration of the acid except in N/100 and N/1000 acid, the zinc being corroded to a greater extent in N/1000 than in N/100 acid. This was noted by Shepherd.

Table of the Data.

TARTARIC ACID

	Tin	Zinc	Copper	Aluminium
N/1	.1677	.1965	.0891	.0024
	.1535	.1906	.0911	.0025
N/10	.5372	.0820	.0823	.0020
	.5363	.0854	.0824	.0019
N/100	.0850	.0275	.0318	.0021
	.0821	.0273	.0309	.0022
N/1000	.0070	.0598	.0039	.0007
	.0072	.0645	.0037	.0007

MALIC ACID

	Tin	Zinc	Copper	Aluminium
N/1	.5865	1.7584	.2086	.0018
	.5875	1.7520	.1907	.0020
N/10	.3660	.1668	.1144	.0015
	.3591	.1672	.1155	.0020
N/100	.0132	.0165	.0237	.0022
	.0132	.0865	.0241	.0015
N/1000	.0010	.0031	.0028	.0007
	.0008	.0033	.0028	.0009

SUCCINIC ACID

	Tin	Zinc	Copper	Aluminium
N/1	.0843	.4429	.1902	.0011
	.0823	.4279	.1955	.0019
N/10	.0127	.1306	.0971	.0015
	.0143	.1230	.0875	.0017
N/100	.0019	.0390	.0107	.0022
	.0020	.0410	.0103	.0011
N/1000	.0007	.0062	.0003	.0003
	.0004	.0063	.0003	.0004

ASPARTIC ACID

	Tin	Zinc	Copper	Aluminium
N/100	.0046	.0205	.0149	.0146
	.0040	.0193	.0151	.0157
N/1000	.0011	.0042	.0014	.0006
	.0012	.0037	.0013	.0007

To explain this apparent irregularity the amount of zinc tartrate corresponding to the amount of acid in the solution was calculated and found to be less than the actual corrosion loss. Assuming the acid to have been entirely used up, the additional corrosion may be due to the action of water on the zinc, which is considerable. A strip of zinc tested in water alone gave a pitted appearance after a slight corrosion coat had been removed. This coating and pitting were also present in the case of zinc and N/1000 acid and account for the greater corrosion found. The coat was also much more adherent than in the other concentrations and seems to have had a catalytic effect on the corrosion.

In some cases however the coating may be protective. This is particularly true in the case of Aluminium.

Aluminium in tartaric acid was corroded only negligibly. Bailey³ has observed this in his work on aluminium. Aluminium has the property of forming a coating of $Al(OH)_3$ on its surface when in contact with a liquid. This coating acts not as a catalyst, but interferes with the direct action of the reagent on the metal. This oxidation, probably by dissolved oxygen, is a type of passivity, and has been observed by Richardson² in connection with the corrosion of iron. Aluminium was also only corroded negligibly in malic, succinic, and aspartic acids. The results are almost identical with those for tartaric acid and show that the oxide coating formed is the only factor in the corrosion of aluminium.

Tin in tartaric acid formed an insoluble product in N/10 acid where a white coating remained on the strips. The corrosion

as a result of this coating was greater than in N acid where the product was soluble and had no opportunity to settle out on the surface of the metal. The product in N/100 and N/1000 was slight and the corrosion loss correspondingly less. Tin in N/100 and N/1000 acid gave more loss than could be accounted for by the amount of acid present. (i.e. as tin tartrate) This is evidence of the formation of some sort of a complex tin tartrate, since tin is not corroded in water at all. A slime or scale on the strips indicated the presence of oxides of tin, which may also have increased the amount of corrosion.

Copper in N/1 and N/10 tartaric acid gave a clear blue solution with a blue product. The strip was clean in N acid but the precipitate adhered in N/10 acid. This may account for the slight difference in corrosion loss between N and N/10 acids. In N/100 and N/1000 a blue solution resulted, but no product was precipitated and the strips were darkened. This oxide coating was ascribed to direct oxidation by the dissolved oxygen, which in the more concentrated solutions was removed by union with the H^+ .

The order of corrosion in tartaric acid was as follows in Table I, the order being that which would be predicted from the electrolytic potentials of the metals. Zinc, most corroded, is more electro-negative than tin, and tin more so than copper. Aluminium is more electro-negative than zinc, but this factor is overcome by the protective coating. The exception to this order in N/10 acid has been explained by the coating formed on tin in N/10 acid which raises its corrosion loss to an abnormal amount. In N/100 acid, tin and copper

precede zinc, possibly due to the formation of the oxide coatings observed on both tin and copper.

Table I.
Order of Corrosion in Tartaric Acid.

<u>Conc.</u>	<u>Order.</u>
N/1	Zn-Sn-Cu-Al
N/10	Sn(Zn-Cu-)Al
N/100	Sn(Zn-Cu-)Al
N/1000	Zn-Sn-Cu-Al

(-- --) indicates practically equal corrosion loss.

MALIC ACID.

Zinc in N/1 malic acid formed a voluminous, white, spongy precipitate. Part of this adhering to the strips, took particles of the metal with it when "peeled" from the strips which were deeply pitted. This product, probably zinc malate hydrolyzed by water, was soluble when more normal malic acid was added. In the other concentrations the product was compact and powdery, and easily brushed from the strips. No pitting was evidenced.

Fin in malic acid formed a clear yellow solution with no precipitate in normal acid. In the other concentrations a white product was formed soluble in normal acid. No coatings adhered. The corrosion varied with the concentration.

Copper in N and N/10 malic acid formed blue solutions with a blue product precipitated which could be removed from the strips when dry, while in N/1000 and N/1000 the strips were darkened slightly and no product was precipitated. The corrosion varied with the

concentration.

The order of corrosion in malic acid is as follows in Table II. The order in N acid follows the electrolytic potentials, but shifts occur in the other concentrations. Copper tends to increase in corrosion loss as compared to zinc and tin.

Table II.

The Order of Corrosion in Malic Acid.

<u>Conc.</u> -----	<u>Order.</u> -----
N/1-----	Zn-Sn-Cu-Al
N/10-----	Sn-Zn-Cu-Al
N/100-----	Cu-Zn-Sn-Al
N/1000-----	(Zn-Cu)(Sn-Al)

SUCCINIC ACID.

Zinc in succinic acid gave an insoluble white product which settled on the strips. The amount of corrosion varied with the concentration from N/1 to N/1000 acid.

Tin in succinic acid formed an insoluble white product and coating. The ammount of corrosion varied with the concentration and in N/1000 acid was negligible.

Copper in succinic acid formed a vivid blue product and solution in N/1 and N/10 acid. These strips were heavily coated with the product. With N/100 and N/1000 acid the solution was light blue and the strips were darkened. No product was precipitated. This fact accounts for the dark oxide coating caused by dissolved oxygen which was prevented in the more concentrated solutions--just as happened with copper in N/100 and N/1000 malic and tartaric acids.

The order of corrosion in succinic acid is as in Table III.

Zinc was corroded most in every concentration. The heavier coating observed on copper indicating a lesser solubility of the copper corrosion product than that of the tin may account for the position of copper ahead of tin, although tin has the greater electrolytic solution pressure.

Table III.

The Order of Corrosion in Succinic Acid.

<u>Cong.</u> -----	<u>Order.</u> -----
N/1-----	Zn-Cu-Sn-Al
N/10-----	Zn-Cu-Sn-Al
N/100-----	Zn-Cu-Sn-Al
<u>N/1000-----</u>	<u>Zn(Cu-Sn)Al--</u>

ASPARTIC ACID.

(The solubility of aspartic acid did not allow the preparation of N/1 and N/10 solutions.)

Zinc in aspartic acid gave a slight white product on the strips which was removed on drying.

Tin gave clear solutions with clean strips. The corrosion was small in each case.

Copper formed clear solutions with an insoluble blue product. The strips were slightly darkened.

Aluminium in N/1000 aspartic acid was negligibly corroded, but in N/100 the corrosion was appreciable. This departure could not be accounted for.

The order of corrosion in aspartic acid is as the electrolytic potentials would predict. in N/1000 solution, but in N/100 the copper may be supposed to form a complex ion with the amino group of the acid, somewhat as it forms the ion $\text{Cu}(\text{NH}_3)_4^{++}$, since copper preceeds tin in this concentration.

Table IV.

The Order of Corrosion in Aspartic Acid.

Conc.-----	Order.-----
N/100-----	Zn-Cu-Al-Sn
N/1000-----	Zn-Sn-Cu-Al

IV.

Discussion.

When the results with the four acids are examined the tendencies in each case are seen to be practically the same. (See tables I-IV) That is in more concentrated solutions, N/1 and N/10, the order of corrosion follows closely the respective electrolytic potentials, except in the few cases where the effect of coatings has been observed. In N/100 and N/1000 solutions, however, shifts occur, the most evident of which is the increased comparative corrosion of copper. A copper oxide coating was formed in every N/100 and N/1000 acid solution. Tin in the same concentrations was often coated with a slime or scale of oxide. The effect of coatings in both concentrated and dilute solutions seems to be catalytic (except in the case of aluminium), and may be best explained by saying that the coating in either a finely divided or colloidal condition, lying against the surface of the metal acts as a sponge to the corrosive reagent,

giving greater concentration than usual at the surface of the metal and increasing corrosion. Copper in this way, on account of its oxide coating, is placed ahead of tin in dilute solutions and sometimes is even ahead of zinc. The heavy coating formed with zinc in normal malic acid is a striking example of the effect of such "spongy" coatings in the more concentrated solutions.

The comparative effect of the acids on the four metals is interesting. (see Table V) One of the factors that influence this order has already been mentioned, namely-the structure of the acid. Tartaric acid with its two hydroxyl groups might be expected to be more corrosive than malic with one hydroxyl and succinic with none. Also the amino group of the aspartic acid would have its effect in some degree. The other factor is the degree of ionization of the different acids. These are given in Table VI and were calculated from the dissociation constants⁵ using Ostwald's Law for ionization As a monobasic acid.

The order of effect on tin and copper in N/100 and N/1000 acids is tartaric, malic, aspartic, succinic. This is in accordance with the degrees of ionization and with the number of OH groups. Tartaric acid is most highly ionized and possesses the greatest number of OH groups. However in N/1 and N/10 and with zinc in every concentration, the order of corrosive effect is changed. This is probably on account of the greater effect of the corrosion products formed in the more concentrated solutions. In these solutions where appreciable coating has been formed the effect is not the same with the

different metals. For example, succinic acid which has the least corrosive action on tin in the more concentrated solutions, is second in its effect on copper and zinc in the same concentrations. This is because of the greater comparative effect of the coatings on copper and zinc in increasing the amount of corrosion.

The effect of the amino group is to place aspartic acid between succinic acid with no OH groups and malic with one.

The formation of complex metallic ions such as the basic copper tartrate by hydrolysis in solutions of low H^+ ion concentration may be a factor in the irregularities noted, but there is nothing positive to indicate their formation.

Table V.
Comparative effect of the Acids on the Metals.

	Zinc	Tin	Copper	Aluminium
N/1	M-S-T--	M-T-S--	M-S-T--	(-----
N/10	M-S-T--	T-M-S--	M-S-T--	-----
N/100	S-T-A-M	T-M-A-S	T-M-A-S	-----
N/1000	T-S-A-M	T-M-A-S	T-M-A-S	-----)

Table VI.
Degrees of Ionization (%)

	N/1	N/10	N/100	N/1000
Tartaric	3.1	9.4	26.3	50.0
Malic	2.0	6.1	18.0	45.0
Aspartic	---	---	10.8	30.2
Succinic	0.8	2.6	7.8	22.5

Summary.

1.- Aluminium is most resistant to corrosion and is only negligibly corroded in such organic acids as tartaric, malic, succinic, and aspartic; probably on account of the formation of a protective oxide coating.

2.- Zinc is least corroded in these acids, followed by tin and copper, though this order is subject to wide changes in certain cases.

3.- Electrolytic solution pressure governs the comparative amount of corrosion of the metals until disturbing factors enter, the most important of which is:

4.- The effect of a coating of the product formed on the metal, which is catalytic to corrosion except in the case of aluminium, by acting as a sponge to the corrosive reagent close to the surface of the metal.

5.- The amount of corrosion increases with the number of hydroxyl groups in dilute solutions of the acids, but in more concentrated solutions the effect of coatings disturbs this.

6.- Corrosion increases with the degree of ionization of the different acids in dilute solutions, but here also in more concentrated solutions this factor is overcome by the effect of the corrosion product.

7.- The amino group increases the corrosive effect of aspartic acid over that of succinic acid, which has neither OH nor NH_2 group.

8.- The evidence of the formation of complexes is negative, although their formation seems possible.

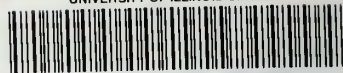
9.- The changing concentration of the acid used, its entire consumption in some instances, the varying types and effects of corrosion products, and the possibility of other disturbing conditions, make the successful application of the manometer cell method for the determination of corrosion rate practically impossible.

V

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